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AN INVESTIGATION OF FACTORS INFLUENCING THE OUTGASSING RATE

Kenneth W. Rogers

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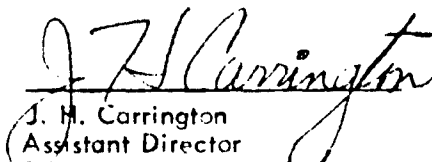
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AN INVESTIGATION OF FACTORS INFLUENCING
THE OUTGASSING RATE

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ABSTRACT

An analysis is made to determine the factors influencing the outgassing from a specimen exposed to a vacuum. Consideration is given to the effect of the specimen temperature and prior exposure to contaminating environments. It is shown that the complete history of the specimen must be considered when estimating the outgassing rate. Two experimental programs were made to determine the constituents of the outgassing of metals. It was found that the outgassing from stainless steel was primarily H_2O , H_2 , and N_2 .

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INTRODUCTION

During the normal operation of a vacuum chamber it is necessary to bring the chamber to atmospheric pressure while test specimens are installed. Upon completion of the installation, the system pumpdown is begun. If it were only necessary to pump the volume of gas contained in the test volume, the pumpdown would be rapid, and for a typical system the ultimate pressure would be approached in a matter of minutes. It is found that this is not the case however, for the pumpdown may require days to reach an ultimate pressure. This extended pumpdown results from large quantities of gas that are bound on the surface layer of the walls and within the walls of the chamber and test specimen. These gases are bound with varying magnitudes of forces and as a consequence under vacuum conditions they are released at varying rates. For several gases, the rate does not become insignificant during an extended pumping period. This results in the walls acting as sources of gases which must be pumped by the vacuum pumps. It is this balance between gases leaving the surface, and gases being pumped that fixes the chamber pressure. In the present report a study is made of various means of changing the rate at which the gases leave the surface.

SOURCES OF GAS

Before discussing means of varying the rate at which molecules leave the wall surfaces, it is useful to discuss the types and origins of some of the typical outgassing molecules.

For purpose of this discussion, two locations of molecules will be considered. These are (1) molecules originally in the wall, and (2) molecules originally in the surface layer.

Molecules In The Wall

This category will include all molecules that must penetrate some thickness of the wall, so it will include those molecules that originate outside the chamber wall, and permeate through the wall into the chamber, as well as those that were originally located in the wall. In many cases it is neither possible nor necessary to distinguish between these two cases, but both will be discussed briefly.

In the case where the molecules were originally in the wall, it is usually found that the behavior can be described by the one dimensional diffusion equations (1) and (2).

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (1)$$

$$N = D \left(\frac{\partial C}{\partial x} \right)_{\text{surface}} \quad (2)$$

Equation (1) is the basic equation that applies throughout the wall, while equation (2) is evaluated at the inner surface of the wall to determine the molecular flux from the wall.

In the case where the molecule must permeate through the wall, Equation (2) still applies, but since the surface gradient is usually unknown, the gradient through the wall is used with an average diffusion coefficient.

$$N = \bar{D} \frac{C_1 - C_2}{L} \quad (3)$$

The concentration C_1 and C_2 should be evaluated on the surface of the wall and not in the gas phases outside the wall, since the surface phenomena whereby the molecules go from the gas phase into the solid may be instrumental in determining the flow rate, however, since the surface concentrations are often unknown, it is common practice to assume the surface phenomena are not limiting, and use the gas phase concentrations to determine the flow rate.

$$N = \bar{D} \frac{C_{1 \text{ gas}} - C_{2 \text{ gas}}}{L} \quad (4)$$

For the vacuum levels to be considered here, the concentration within the chamber may often be neglected.

It is found that the physical description of the flow of gas molecules in a wall varies with the molecular structure of the wall. For structures like metals, the gas molecule must go into solution with the wall molecules in order to diffuse through the wall. Thus, for example hydrogen diffuses through metals in the atomic form, and must join another hydrogen atom on the inner surface before it can leave the wall as a molecule of hydrogen.

This requirement that the gas be soluble in the metal limits the gases that can diffuse through a metal wall. The most notable examples of gases that do not diffuse through metal walls are the noble gases which do not form chemical bonds.

On the other hand diffusion in structures such as glass, plastics, rubber, etc. does not require formation of a solution, and these materials are readily permeated by helium for example.

In both cases the movement of the gas molecules within the walls is the result of a series of random motions. These motions result when the random thermal oscillations of the molecule reach a sufficiently high level to activate the molecule and overcome the bond between the molecule and its site in the wall. A simple equation, the Arrhenius rate equation, is generally used to determine the fraction of the molecules with thermal energy in excess of the activation energy. Since this represents the fraction of molecules in the process of moving from one site to another, this is also representative of the diffusion coefficient and it is found that the diffusion coefficient can be approximated by

$$D = D_0 \exp \left(-\frac{E}{RT} \right) \quad (5)$$

Thus, reducing the temperature reduces the fraction of molecules with thermal energy in excess of the activation energy, and therefore reduces the diffusion coefficient. Conversely increasing the temperature increases the diffusion coefficient. If other conditions are fixed, the outgassing rate is directly proportional to the diffusion coefficient so this represents one method of varying the outgassing rate.

Molecules In The Surface Layer

This category will include the molecules that are adsorbed on the wall surface, and the molecules that are contained within any films or oxide layers on the wall surface.

Many experiments have been made demonstrating that molecules of a gas will be adsorbed on the surface of a solid. In these experiments it is found that the bond between the adsorbed molecule and the wall varies with the amount of wall surface that is covered with adsorbed molecules. When the surface coverage is small, the bond is often stronger

than when the surface coverage is large. The surface coverage is generally discussed in terms of the fraction of the surface that is covered and the minimum condition of complete coverage corresponds to a layer of adsorbate one molecule deep called a monolayer of adsorbate. As the quantity adsorbed is increased beyond a monolayer to several layers, the bond approaches that of the liquid phase of the adsorbate. If the bond is stronger at the lower coverage, the vapor pressure of the gas over the wall will be lower than the corresponding vapor pressure over the liquid phase of the adsorbates. It is possible to have one or more monolayers of molecules adsorbed on a surface at a pressure that is only a fraction of the vapor pressure required over the liquid phase of the adsorbates.

While there are several general types of adsorption curves (Reference 1), the characteristics just described are well illustrated by the curves of Figure 1, where the qualitative behavior of the surface coverage is presented as a function of temperature and pressure. Here it is seen that increasing the pressure increases the surface coverage, while increasing the temperature decreases the surface coverage. This is the result of the dynamic balance that exists at equilibrium, when the number of molecules being adsorbed on the wall must equal the number of molecules being desorbed from the wall. Increasing the pressure increases the rate at which molecules of the gas strike the surface, so if a fixed fraction of those striking are adsorbed, the rate of adsorption increases. To maintain equilibrium, the rate of desorption must increase, but if a fixed fraction of the covering molecules are desorbed per unit time, the balance can only be maintained by an increase in the coverage. Actually this line of reasoning leads to the linear relationship between coverage and pressure which often exists at low coverage. At higher coverage, the fraction of the available molecules adsorbed and desorbed varies with the coverage and this gives more complicated relationships. The effect of increasing the temperature is to increase the kinetic energy of the molecules, and reduce the fraction of those incoming molecules that are adsorbed. This then requires an increase in the surface coverage

to maintain equilibrium. It is found experimentally that the temperature dependence can be approximated by an equation of the form used in the diffusion equation $D = D_0 \exp(-\frac{E}{RT})$

While the discussion so far has considered the surface to be covered with only a few layers of gases, the experimental data obtained from the outgassing of vacuum chambers indicate that quantities of gases corresponding to tens of monolayers are pumped from the chamber. While these gases could be originating within the chamber wall, and not in the surface layer, one strong argument against this is based on the following experimental observation. It is often found (Reference 2 and 3), that if a vacuum chamber is exposed to a moist atmosphere before evacuation, there is a larger quantity of outgassing than if the chamber is exposed to a dry atmosphere. This additional outgassing appears to be water vapor, so it would seem that the gas must be attached to the surface layer and not diffused into the chamber wall, since water vapor would not be expected to go into solution with the wall. Dayton (Reference 4) has suggested that this water vapor is maintained within the capillaries of a surface oxide layer. Thus the surface coverage of the capillary walls could be less than a monolayer and there would still be an outgassing quantity corresponding to tens of monolayers if the area is based on the chamber surface area with no consideration given to the additional surface area due to the capillaries. Thus if this is the mechanism, the apparent discrepancy in the number of monolayers can be resolved by accounting for the additional surface area of the capillary walls.

It is shown in Reference 4 that for a typical case the same diffusion Equations (1) and (2) apply to the oxide layer if only one geometry of capillary is involved. If there is a distribution of geometries, it is necessary to apply Equations (1) and (2) to each geometry and sum the results of all geometries. It is further found that for any one geometry the form of the diffusion coefficient is again $D = D_0 \exp(-\frac{E}{RT})$.

From this brief discussion of the outgassing of the molecules located both in the wall, and in the wall surface layer, it is apparent that there are two main parameters that govern the outgassing rate, these are (1) the concentration gradient at the surface and (2) the diffusion coefficient. These are the parameters that must be varied to change the outgassing rate. In the following sections, equations (1) and (2) will be discussed for various boundary and initial conditions to determine the effects of these conditions on the concentration gradient and the diffusion coefficient.

SOLUTIONS TO DIFFUSION EQUATIONS

Since the diffusion equation has been widely studied in problems of heat conduction, it is useful to examine the analogy between heat conduction and outgassing so existing heat conduction solutions can be applied directly to the outgassing problem.

Heat Conduction Analogy

Using the notation of Carslaw and Jaeger (Reference 5) the heat conduction equations that are analogous to Equations (1) and (2) are, respectively,

$$\frac{\partial v}{\partial t} = \frac{1}{\rho c} \frac{\partial}{\partial x} \left(K \frac{\partial v}{\partial x} \right) \quad (6)$$

$$q = K \left(\frac{\partial v}{\partial x} \right)_{\text{surface}} \quad (7)$$

In the case where the density, specific heat, and thermal conductivity can be assumed independent of the temperature, Equations 6 and 7 can be written.

$$\frac{\partial v}{\partial t} = k \frac{\partial^2 v}{\partial x^2} \quad (8)$$

Where k is the thermal diffusivity. Similarly, if the diffusion coefficient can be assumed independent of the concentration, Equation 1 can be written

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (9)$$

While these assumptions are not required in order to develop the analogy, the development and subsequent mathematics, are simplified, and since these assumptions are valid for many conditions they will be retained for the remainder of this report.

Clearly in these equations, the temperature rise (v) corresponds to the concentration (C) and the thermal diffusivity (k) corresponds to the diffusion coefficient D , while the heat flux q , corresponds to the outgassing rate N . Similarly, the boundary conditions of heat conduction can be applied.

As an example, consider the simple heat conduction problem of a semi-infinite plate having a uniform initial temperature (v_0) with the surface temperature changed to zero at time $t = 0$. This corresponds to a semi-infinite plate having a uniform initial concentration (C_0) of gas molecules with the surface concentration reduced to zero at time $t = 0$. These conditions would exist if the plate were suddenly exposed to a pump

that captured each molecule as it left the plate surface. The solution to the problem is (Page 59, Reference 5)

$$C = C_o \operatorname{erf} \left(\frac{x}{2 \sqrt{Dt}} \right) \quad (10)$$

$$\text{where } \operatorname{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-z^2) dz$$

$$N = D \left(-\frac{\partial C}{\partial x} \right)_{x=0} = C_o \sqrt{\frac{D}{\pi t}} = C_o \sqrt{\frac{D}{\pi t}} \quad (11)$$

Equation 11 illustrates the variation of the outgassing rate with the initial concentration and diffusion coefficient. It also shows that the outgassing rate will change with the time since the pumping started.

While this configuration is readily analysed, in practice, the plate thickness will be finite instead of semi-finite, and the pump will not capture each molecule that leaves the surface. It is useful to determine what conditions are required for the semi-infinite configuration to represent a practical approximation.

It would be expected that for a time after the outgassing process is begun, the effects of the change in surface concentration would be essentially limited to a region near the surface. This is borne out in Figure 2 which is a plot of Equation 10 showing the change in concentration with both pumping time and distance into the plate. It is clear that for values of the parameter $\frac{x}{2 \sqrt{Dt}} > 2$ the concentration is essentially unchanged,

and consequently for values of pumping time $t \leq \frac{x^2}{16D}$ the effects of the wall thickness beyond x are negligible. Thus, if the wall had a thickness equal to L , the effect of the finite thickness would not be significant for pumping time $t \leq \frac{L^2}{16D}$, if no molecules escaped from the wall at $x = L$. This latter condition would be closely approximated if there was no pumping on that surface. In the heat conduction analogy, this corresponds to a wall insulated at L . Thus it is concluded that the semi-infinite approximation is adequate for pumping time $t \leq \frac{L^2}{16D}$.

The effect of a limited pumping capacity can be assessed by considering the following model. If the outgassing walls are the walls of an evacuated chamber, the outgassing will be removed by the pumping system but the finite volume flow rate of the pump must be included in the boundary condition. Since the rate at which the molecules are removed by the pump will depend not only on the speed of the pump, but also on the gaseous concentration in the chamber, the approximate boundary condition becomes

$$N = D \left(\frac{\partial C}{\partial x} \right)_{x=0} = \left(\frac{C_{x=0}}{C_{\text{gas}}} \right) \frac{S}{A} = \phi C_{x=0} \quad (12)$$

Where S is the system pumping speed for the gas being considered, A is the area of the outgassing surface, and $\left(\frac{C_{x=0}}{C_{\text{gas}}} \right)$ is the ratio of surface concentration to gas concentration, evaluated when the wall is in equilibrium with the surrounding gas. This term is required to account for the increase in concentration implied by Figure 1, which shows that a surface concentration approaching the liquid state may be in equilibrium with a gas at a pressure even less than the vapor pressure. Thus at times the ratio $\left(\frac{C_{x=0}}{C_{\text{gas}}} \right)$ may be on the order of 10^3 . It is assumed that the terms in ϕ are not significantly altered by changes in concentration.

This boundary condition in Equation 12 is analogous to the "radiation" or "surface heat transfer coefficient" boundary condition in heat conduction.

$$q = K \left(\frac{\partial v}{\partial x} \right)_{x=0} = H v_{x=0} \quad (13)$$

The solution to the problem is (Page 71, Reference 5)

$$N = C_o \phi \left\{ \exp \left[\left(\frac{\phi}{D} \right)^2 Dt \right] \left[1 - \operatorname{erf} \left(\frac{\phi}{D} \sqrt{Dt} \right) \right] \right\} \quad (14)$$

In a fairly typical case, the parameter ϕ/D may be evaluated by assuming

$$\frac{C_{x=0}}{C_{\text{gas}}} = 10^3 ; \quad \frac{S}{A} = 10 \text{ (cm/sec)} ; \quad D = 10^{-10} \text{ (cm}^2\text{/sec)}$$

$$\text{Then } \frac{\phi}{D} = 10^{-8} \text{ (cm}^{-1}\text{)}$$

Thus the parameter $\left(\frac{\phi}{D} \right) \sqrt{Dt} \approx 1$ if $t \approx .01$ sec. In this case Equation 14 can be expanded to

$$N = C_o \phi \exp \left[\left(\frac{\phi}{D} \right)^2 Dt \right] \frac{\exp \left[- \left(\frac{\phi}{D} \right)^2 Dt \right]}{\sqrt{\pi}} \left[\frac{1}{\frac{\phi}{D} \sqrt{Dt}} - \frac{1}{2 \left(\frac{\phi}{D} \right)^3 (Dt)^{3/2}} + \dots \right] \quad (15)$$

$$\approx C_o \sqrt{\frac{D}{\pi t}} \left[1 - \frac{1}{2 \left(\frac{\phi}{D} \right)^2 Dt} \right] \quad (16)$$

From this equation it can be seen that in the typical application, the effect of a limited pumping speed is negligible. This is due to the small fraction of the incident molecules that are able to diffuse back into the wall.

Having established some limits on the applicability of the semi-infinite plate analysis it is useful to examine the implications of Equation 11

$$N = C_o \sqrt{\frac{D}{\pi t}}$$

Since for most applications the chamber pressure is directly proportional to the outgassing rate, this expression shows the functional relationship between the chamber pressure and the variables, diffusion coefficient, pumping time and initial concentration. The chamber pressure will be reduced by (1) reducing the diffusion coefficient, (2) increasing the pumping time, (3) decreasing the initial concentration. These factors will be considered individually.

Diffusion Coefficient

Since the outgassing rate is proportional to the square root of the diffusion coefficient, a reduction in the diffusion coefficient will be reflected in a lowered outgassing rate, and a lowered chamber pressure. It was noted in Equation 5 that the diffusion coefficient was approximately proportional to $\exp(-E/RT)$. Since decreasing the temperature (T) of the wall increases the exponential term, it would be expected to cause a large reduction in the outgassing rate. Reference 6 shows this has been verified at a condition between room temperature and liquid nitrogen temperature for the case of hydrogen diffusion from stainless steel walls. It is also implicitly verified in many chambers when it is found that the chamber pressure drops significantly when the cold shroud is cooled to liquid nitrogen

temperature. In this case, part of the pressure drop comes from the cryopumping action of the cold shroud, but since at low outgassing rates hydrogen is a major fraction of the outgassing and it is not cryopumped on the shrouds, it follows that the outgassing rate must be decreased by the cooling.

Pumping Time

Since the analysis shows that the outgassing rate is inversely proportional to the square root of the pumping time, it appears that the outgassing rate and consequently the chamber pressure can be reduced to any value by increasing the pumping time. Unfortunately, since the significant change in the pressure level is a decade, which requires two decades of pumping time, it is not practical to achieve pressures that are significantly lower than those attained after 1 - 10 hours of pumping.

It is possible to partially avoid this problem by varying the diffusion coefficient during the pumping. For example by heating the chamber walls, and increasing the diffusion coefficient, the outgassing rate is increased. If these conditions are maintained for a period of time, the concentration near the surface of the wall will be reduced significantly. If the chamber walls are now cooled to the original temperature, the outgassing rate will drop due to the local reduction in concentration. This is the principle involved in the usual bake out of a chamber.

This process can be described analytically by considering the diffusion coefficient to be time dependent. In the case of the semi-infinite plate, the equation for the outgassing rate will be given by Reference 7.

$$N = D \left(\frac{\partial C}{\partial x} \right)_{x=0} = D \frac{C_0}{\sqrt{\pi \lambda}} \quad (17)$$

where $\lambda = \int_0^t D dt$

Thus the heating causes a large increase in the diffusion coefficient, and that part of the pumping time dominates the τ term even after the system has been returned to room temperature. This is illustrated in Figure 3, which shows the parameter τ and the outgassing rate as a function of that pumping time for a typical bakeout. A temporary increase in the diffusion coefficient has a similar end result as an increase in pumping time in that they both decrease the outgassing rate. It is inconsequential whether the τ term is increased by a large value of the diffusion coefficient or a large pumping time.

Since a typical bakeout involves heating the chamber to high temperatures it is useful to determine whether the heating process can be made more effective. In the case of the usual diffusion of gases from within the chamber wall, the diffusion coefficient is so low that only the inner fraction of the wall is influenced by the outgassing during short pumping times. Similarly those gases within the surface layer are only influenced by the local condition at the surface of the wall. Thus one method of improving the bakeout procedure would be to increase the effects of the bakeout at the inner surface of the chamber. This could possibly be done by heating the walls from within the chamber, with a pulsing source of heat so the inner surface temperature would experience a sudden rise, followed by a gradual decline as the heat was conducted into the wall. This form of heating would keep the inner surface at a temperature above the average temperature of the wall, in turn keeping the surface diffusion coefficient above the average diffusion coefficient of the wall. This would increase the quantity of gas removed from the inner layer over that which would have been removed if the wall temperature had been uniform. This will produce a non-uniform concentration in the wall, but due to the slow diffusion rate, the less thoroughly baked outer layer of the wall will not have an immediate influence on the outgassing rate. The effect of this gradient will be to reduce the rate at which the outgassing is decreasing.

Since this analysis of this pulsing bakeout would be very involved, approximations will be made and the process will be analyzed in two steps. It will be assumed that the inner chamber wall surface temperature can be used as the characteristic temperature of the inner layer, therefore, the first step will be to determine the ratio of the surface temperature rise to the average wall temperature rise, and the second step will estimate the effect of the increased surface temperature on the outgassing rate.

One method of supplying a pulsing source of heat would use radiant energy from a light source. During operation the light would be on for a period of time, and off for a period of time. The length of these periods and the light intensity would be adjusted to maintain the required average heat flux.

The average heat flux would be

$$\bar{q} = \frac{1}{\tau} \int_0^{\tau_h} q \, dt = q \frac{\tau_h}{\tau} \quad (18)$$

Here τ is the period of the cycle, and τ_h is the heating part of the cycle where the heat flux is maintained at q . While it would be desirable to determine the variation in the ratio of the surface temperature to the average temperature as a function of the cycle parameters q , τ_h , τ and the number of cycles that have been made, this ratio will be examined only for the first cycle to determine the magnitude of any benefits. Since the wall will be assumed to be at a uniform temperature initially, this analysis will strictly apply only to the first cycle, but it will be a good approximation for all cycles if the cycle period is long enough to allow the thermal gradients to be negligible.

Since the thermal diffusivity is orders of magnitude greater than the molecular diffusion coefficient, it is not possible to use the semi-infinite plate assumption for the heat conduction analysis. The wall will be considered of thickness L and the outer surface of the wall will be assumed to be insulated.

The conditions can be summarized -

$$\begin{aligned} T - T_0 &= 0 & t < 0 \\ \left(\frac{\partial T}{\partial x}\right)_{x=0} &= \frac{q}{K} & 0 < t < \tau_h \\ \left(\frac{\partial T}{\partial x}\right)_{x=0} &= 0 & \tau_h < t < \tau \\ \left(\frac{\partial T}{\partial x}\right)_{x=L} &= 0 & \text{all } t \end{aligned}$$

After some manipulation, the appropriate solution for the surface temperature rise can be obtained from Page 127 Reference 5.

$$(T - T_0)_{x=0} = \frac{qt}{\rho c L} + \frac{Lq}{K} \left[\frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp\left(-k \left(\frac{n\pi}{L}\right)^2 t\right)}{n^2} \right] \quad (19)$$

$0 < t < \tau_h$

$$(T - T_0)_{x=0} = \frac{q\tau_h}{\rho c L} + \frac{Lq}{K} \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp\left[-k \left(\frac{n\pi}{L}\right)^2 (t - \tau_h)\right] - \exp\left[-k \left(\frac{n\pi}{L}\right)^2 t\right]}{n^2} \quad (20)$$

$\tau_h < t < \tau$

While the average wall temperature varies during the cycle, for the case when the heating time is a small fraction of the total cycle, the average temperature rise can be approximated by

$$\bar{T} - T_0 = \frac{q\tau_h}{\rho c L} \quad (21)$$

The ratio of the surface temperature rise to this average wall temperature rise becomes

$$\frac{(T - T_o)_{x=0}}{(T - T_o)} = \frac{t}{\tau_h} + \frac{L^2}{k \tau_h} \left[\frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp\left(-k \left(\frac{n\pi}{L}\right)^2 t\right)}{n^2} \right] \quad (22)$$

$0 < t < \tau_h$

$$\frac{(T - T_o)_{x=0}}{(T - T_o)} = 1 + \frac{L^2}{k \tau_h \pi^2} \sum_{n=1}^{\infty} \frac{\exp\left[-k \left(\frac{n\pi}{L}\right)^2 (\tau_h - t)\right] - \exp\left(-k \left(\frac{n\pi}{L}\right)^2 t\right)}{n^2} \quad (23)$$

$t > \tau_h$

These have been evaluated for a 1/4" thick stainless steel wall and the results are presented in Figure 4. From this figure it is apparent that the pulsing technique can significantly raise the surface temperature above the average wall temperature only if the duration of the pulse is short. It is also apparent that since the surface temperature approaches the average temperature about 2 sec after the termination of heating, the thermal gradients are small so if the cycle period is greater than 2 sec this analysis will apply for all cycles.

The effects of the temperature pulses on the outgassing can be estimated by comparing the values of γ for a pulsed wall, with the values for a wall at the average wall temperature. In the case of the pulsed wall, the values of γ would be evaluated using the surface temperature (T_s).

$$\gamma_s = \int_0^{\tau} D_s dt = D_o \int_0^{\tau} \exp\left(-\frac{E}{RT_s}\right) dt \quad (24)$$

When the expressions for surface temperature are obtained from Equation 22 and 23 and substituted into Equation 24, the resulting equation must be solved numerically. In order to do this it is necessary to make some assumption about the magnitude of the heating rate and the activation energy. During a typical bake out the temperature rise rate may be about 360°K per hour or about .1°K per cycle if the cycle time is 1 sec. This has been used with an activation energy of 20,000 cal/mole to evaluate Equation 24, and the results are plotted in Figure 5. In this figure $\bar{\tau}$ has been ratioed to $\bar{\tau}_0$ where

$$\bar{\tau} = D_0 \left[\exp \left(- \frac{E}{RT} \right) \right] \tau \quad (25)$$

It is apparent that the bake-out cycle will be improved significantly only if the heating pulse time is extremely short, on the order of 10^{-7} sec. Unfortunately this short pulse requires large transient power handling capabilities. For example using the 1/4" stainless steel plate with a .1°K temperature rise per cycle with a one second period requires a steady state heat flux of .23 watt/cm², but if the heating pulse is 10^{-7} sec, then the transient power becomes 2.3×10^6 watt/cm². The magnitude of this power handling requirement can be appreciated by calculating the temperature required for the radiating device. If the radiator has the same area as the chamber, and an emissivity of unity the temperature can be approximately determined from

$$q = 5.67 \times 10^{-12} T^4 = 2.3 \times 10^6$$

or $T = 2.5 \times 10^4 \text{ } ^\circ\text{K}$ (26)

Thus the temperature required to generate the desired heat pulse is too high to be practical even with the favorable assumptions of a radiating surface area equal to the chamber area and an emissivity equal to unity. It is considered that this pulsing technique does not

present a practical means of increasing the surface diffusion coefficient during the bake out of the chamber wall.

The previous analysis was only concerned with increasing the diffusion coefficient, and did not consider the possibility that the heat pulse might be used to desorb a surface layer of molecules. When this study was initiated it was planned to investigate the possibility of using light sources to desorb any monolayers of molecules from the wall. It was felt that there would be a good probability that some of the incident radiation would be first absorbed by the gas molecules before being transmitted to the wall. If enough was absorbed, the molecular energy would exceed the activation energy and the molecule would be desorbed. It was found that this approach was being investigated by Lange and Riemersma in Reference 8. In their preliminary findings they noted that while some of the incident radiation was absorbed by the gas molecules, the yield in terms of desorbed molecules/unit power was very small, being about 2×10^{-10} molecules/photon. Since this would require about .6 Kw hr/cm² to desorb a monolayer of adsorbed gas, it was not felt that this approach to desorption warranted further study.

Initial Concentrations

Equation 11 shows that the outgassing rate is directly proportional to the initial concentration so it is important to determine how the concentration can be varied.

In the preceding sections it was found that the effect of a bakeout was to temporarily increase the diffusion coefficient so the higher outgassing rate would reduce the concentration of gases in the walls. Clearly a thorough bakeout would leave the walls with a low concentration and presumably if the chamber pressure was raised to atmospheric pressure for a short time to install a test object, the slow diffusion coefficient would prevent

the chamber wall from being recontaminated to the original concentration. Thus the subsequent pumpdown should show a lower outgassing rate due to the lower initial concentration. Since all chamber operations involve this cycle of exposure to air, pumpdown, exposure to air again etc. it is necessary to determine the effects of these cycles on the outgassing rate in order to estimate the time required to pump the chamber to a specific pressure level.

The analysis would be simplified if it could be assumed that the chamber wall was initially at a uniform concentration. If the wall had just been thoroughly baked and outgassed the concentration could be considered zero throughout the wall, while if the wall had been exposed to gasses for an extended period of time, the concentration would be uniform at the equilibrium value associated with the gas concentration. In general neither of these conditions will exist since the exposure times will often be short compared to the time required to establish a uniform concentration, and the outgassing rate will depend upon the exposure history of the chamber over several of the preceeding cycles. Since there are wide variations of possible exposure histories, it will be useful to analyse a typical history that demonstrates the effects of these variations.

Often in the operation of a chamber, the chamber may first be baked and thoroughly outgassed so the concentration is negligible, and then the chamber is exposed to a gas atmosphere while an experiment is installed. During this time period the surface concentration will be C_0 . Following this, the chamber is pumped down, reducing the surface concentration to zero. At the completion of this test, the chamber may again be exposed to a comparable gas atmosphere, while experiments are changed, and then the pumpdown is started again. Now if the time required to introduce and remove the bulk of the gases is small compared to both the gas atmosphere exposure time and the time spent under vacuum conditions, the exposure-pumping process may be regarded as a series of step functions where the surface

concentration changes between 0 and C_0 . In this case the initial and boundary conditions can be summarized.

$$\begin{array}{lll}
 C = 0 & \text{all } X & t < 0 \\
 C = C_0 & X = 0 & 0 < t < t_{g1} \\
 C = 0 & X = 0 & t_{g1} < t < t_{v1} \\
 C = C_0 & X = 0 & t_{v1} < t < t_{g2} \\
 C = 0 & X = 0 & t_{g2} < t < t_{v2}
 \end{array} \quad (27)$$

Where t_{g1} corresponds to the time the first gas exposure ended, and t_{v1} corresponds to the time the first vacuum exposure ended etc. The solution to the diffusion equations using these conditions can be obtained from pages 63 of Reference 5.

$$\frac{C}{C_0} = \operatorname{erfc} \frac{X}{2(Dt)^{1/2}} - \operatorname{erfc} \frac{X}{2[D(t - t_{g1})]^{1/2}} \quad t_{g1} < t < t_{v1} \quad (28)$$

$$\begin{aligned}
 \frac{C}{C_0} = & \operatorname{erfc} \frac{X}{2(Dt)^{1/2}} - \operatorname{erfc} \frac{X}{2[D(t - t_{g1})]^{1/2}} + \operatorname{erfc} \frac{X}{2[D(t - t_{v1})]^{1/2}} \\
 & - \operatorname{erfc} \frac{X}{2[D(t - t_{g2})]^{1/2}} \quad t_{g2} < t < t_{v2}
 \end{aligned} \quad (29)$$

Where $\operatorname{erfc} y = 1 - \operatorname{erf} y = 1 - \int_0^y e^{-z^2} dz$

The molecules diffusing from the wall can then be calculated

$$N = -\left(\frac{D}{\pi}\right)^{1/2} C_0 \left[t^{-1/2} - (t - t_{g1})^{-1/2} \right] \quad t_{g1} < t < t_{v1} \quad (30)$$

$$N = -\left(\frac{D}{\pi}\right)^{1/2} C_0 \left[t^{-1/2} - (t - t_{g1})^{-1/2} + (t - t_{v1})^{-1/2} - (t - t_{g2})^{-1/2} \right] \quad t_{g2} < t < t_{v2} \quad (31)$$

While each term in the resulting equations shows the same square root relationship between the outgassing rate and time that was found in Equation 11, the equations must be evaluated more carefully to determine the effects of the series of terms.

Considering only the pumpdown immediately following the initial gas exposure, two limiting conditions can be noted. If the equation is evaluated when the pumping time is short compared to the exposure time, the $(t - t_{g1})^{-1/2}$ term dominates. Since $t - t_{m1}$ is the pumping time, this result is the same as Equation 11. On the other hand if the equation is evaluated after long pumping times compared to the exposure time, a $(t - t_{g1})^{-3/2}$ term dominates and the equation no longer resembles the usual diffusion equation. This result is shown in Figure 6 where the relative outgassing rate has been calculated for a series of exposure times. In this and the following figures, the outgassing rate has been ratioed to the parameter $(\frac{D}{\pi})^{1/2} C_0$.

If the system has a pumping speed that is independent of pressure, Figure 6 can be used to estimate the relationship between the exposure time and the pumping time required to reach a specific pressure level. When this is done for a typical range of pumping and exposure times, it is found that the required pumping time is proportional to the exposure time raised to the 1/2 to 2/3 power. Thus doubling the exposure time should increase the pumpdown time by about 50%.

If the initial gas exposure time was very long compared to the time of interest, the concentration can be considered uniform, and the first pumpdown will exhibit the square root relationship between outgassing rate and pumping time. If the system is now exposed to a gas atmosphere, and again pumped down, the resulting outgassing variation will depend upon both the previous pumpdown time and the following gas atmosphere exposure time. Examples of the resulting outgassing variations are shown in Figure 7 for a range of initial pumping times which have been followed by a unit exposure time. The general pattern of

the outgassing curve, is to follow the thoroughly outgassed curve until the outgassing rate is of the same order of magnitude as that at the end of the prior pumpdown at which point the curve flattens out approaching the prior pumpdown curve, but always lagging behind it by a time interval equal to the sum of the exposure time and the present pumping time. This return to the square root relationship serves to emphasize that the unit exposure and subsequent pumpdown represent only a relatively small variation in the general pumpdown of a semi-infinite plate. This can be seen in Figure 8 where the curve with a 10% unit initial pumpdown time has been replotted so the time scale includes the initial pumpdown and exposure. Here it is seen that the unit exposure and the subsequent pumpdown occupy only a small fraction of the logarithmic plot, and it is also evident that the pumpdown will continue along the original curve, despite additional minor exposures. Each succeeding pumpdown will produce an outgassing rate only slightly below that of the previous pumpdown, and since the pressure is directly related to the outgassing rate, enormous pumping times would be required to significantly reduce the system base pressure. This is the same problem discussed in the section on pumping where it was shown that in practice this difficulty is overcome by baking the chamber, thus increasing the diffusion coefficient enough to remove the gas from the finite walls. Once the system has been baked and cooled, the slow diffusion rate will delay any significant ingassing, and the analysis for the thoroughly outgassed system will apply. This emphasizes that the outgassing characteristics of a system are dependent upon the complete exposure history of the system, and not just the conditions immediately preceding the pumpdown.

EXPERIMENTAL PROGRAM

When this study was initiated there were several areas where experimental data was lacking. An article by Dayton, Reference 9 summarizing the outgassing data to 1959 presented the results of the outgassing measurements on many materials. These results were obtained by pressure measurements, and consequently did not specify the species of gases that were outgassing. Since the details of the outgassing process depend upon the gases involved it was decided to attempt to measure the outgassing species for some common metals using a mass spectrometer.

The measurement of the outgassing rate can be done by several methods. In the constant volume method, the specimen is placed in a chamber of known volume, and the rate of pressure rise in the chamber is noted as the specimen outgasses. The outgassing rate is then determined by

$$N = \frac{N_A}{M} \frac{V_{\text{chamber}}}{A_{\text{specimen}}} RT \frac{dp}{dt} \quad (32)$$

While this system is simple in concept it has some drawbacks. One problem is the possibility that some of the gases will be adsorbed on the walls of the chamber, and reduce the chamber pressure rise rate. This problem is aggravated by the fact that the speed for this type of pumping changes with the quantity that has been pumped so it is very difficult to analyze the results. Another problem is the possibility that the mass spectrometer will act as a pump and remove some of the gases.

Another measuring technique uses a dynamic system with a chamber continuously pumped by a pumping system of known speed. In this case the outgassing rate is given by

$$N = \frac{N_A}{M} \frac{P - P_0}{A_{\text{specimen}}} RT S \quad (33)$$

This system requires careful pumping speed determination and will be subject to the wall adsorption problems previously discussed, unless the outgassing rate has been nearly constant for the time period required to achieve equilibrium between the adsorption and desorption on the chamber walls.

Perhaps the most satisfactory way to measure the outgassing would be to surround the specimen with a pumping surface that would capture each molecule of gas as it struck the pump. Thus the only molecules arriving at the mass spectrometer would be those coming directly from the test specimen to the mass spectrometer. As shown in Reference 10 the radiation factors of radiant heat transfer can be used to determine the fraction (ψ) of the molecules leaving one surface that will pass directly to another surface. The outgassing rate can then be determined from

$$N = .0533 \frac{N_A}{(MT)^{1/2}} \frac{P_{(torr)}}{\psi A_{\text{specimen}}}$$

Unfortunately there is no practical pumping surface capable of capturing each incident molecule, and some fraction of the molecules would rebound from the pump into the mass spectrometer. However, the cryopump does capture a large fraction of the incident molecules and if the capture probability is high enough, the fraction of the molecules entering the mass spectrometer after a collision with the pumping surface will be negligible compared to those molecules passing directly into the mass spectrometer. This system will still suffer from any adsorption on the walls of the mass spectrometer tube, since these adsorbed molecules would not contribute to the measured pressure. This problem could be avoided or at least reduced by using a mass spectrometer that can be mounted in the chamber like a nude ionization gage.

Based on these considerations of the different methods it was decided to use the cryopumping approach with the experimental arrangement shown in Figure 7. In this arrangement the cryopump was cooled with gaseous helium to about 25°K so the hydrogen could not be pumped by the cryopump. The hydrogen was to be pumped by a separate diffusion pump, but due to the small passages from the test arrangement to the diffusion pump it was not possible to use the diffusion pump speed to estimate the hydrogen flow rate, so the hydrogen data would only be qualitative. As shown in Figure 7 provision was made to cool the specimen with liquid nitrogen. This was done in an attempt to avoid another problem encountered in measuring the initial outgassing species. This is the time delay between commencing pumpdown and obtaining useful mass spectrometer data. This delay results from the necessity for baking out the mass spectrometer tube to assure that the measured outgassing does not result from the tube itself. Unfortunately this bakeout requires several hours and during this time period the test species will be outgassing and some of the species may be diminishing so the results are not indicative of the initial outgassing. It was hoped to avoid this problem by cooling the test specimen to low temperatures while the mass spectrometer was baking out. Presumably if the specimen temperature is low enough, the diffusion coefficient would be too small to allow any significant quantity of gas to escape during the bakeout. Once the bakeout is completed, by bringing the test object to the desired temperature the approximate initial outgassing could be observed. While this will only approximate the initial outgassing, it should be a good approximation since as discussed in the section on pumping time, when the diffusion coefficient is time dependent, the parameter τ is more significant than pumping time, and the parameter τ evaluated during the time the specimen is cold, will be negligible compared to the value after a few seconds at room temperature. One problem with this approach is the possibility that the cold

test specimen will absorb gases coming from the mass spectrometer during bakeout, and these gases will be desorbed when the specimen is warmed up, giving an incorrect outgassing rate.

In the experimental results from this arrangement it was found that despite the presence of the cryopump, the quantities of two of the most prominent gases, nitrogen and water vapor, were virtually unaffected by the temperature of the specimen. Thus the pressure level was established by something other than the specimen. It was found that the nitrogen level was sensitive to the pressure in the liquid nitrogen cooled shroud and a subsequent investigation revealed a small leak in a coupling. Unfortunately the time scheduled for these tests did not permit a correction of this problem. No simple explanation could be found for the large quantity of water vapor that was entering the mass spectrometer tube, however, some of it appeared to be associated with the nude ionization gauge located near the mass spectrometer. This was evidenced by the rise in the quantity of water vapor when the nude gage was turned on. Figure 10 illustrates the typical behavior of gas pressure when the nude gage was turned on and when a copper specimen was warmed to room temperature. Since the mass spectrometer has not been fully calibrated the pressure listed is the equivalent nitrogen reading, that is the pressure of nitrogen required to produce the same output on the mass spectrometer. It is clear that the background of the gases is of the same order as the change that is produced when the specimen is warmed. There are small rises in hydrogen and water vapor when the specimen is warmed. While some of the water vapor may have been cryopumped by the specimen during the mass spectrometer bakeout, the water vapor outgassing rate calculated from the pressure rise is of the order of 10^{-7} torr liters/sec-cm², which is in the range of values reported in the literature for total outgassing of other metals during the first hour of pumping. Due to the unknown pumping speed for hydrogen no estimates were made for the outgassing rate that would be required to generate the hydrogen pressure rise.

It is emphasized that the level of the nitrogen could be varied by changing the shroud pressure, and therefore that level is not considered significant.

Since time did not permit correcting the experimental difficulties, it was decided to investigate the possibility of using the constant volume technique to measure the outgassing species.

Initial experiments were made to determine the outgassing of the chamber shown in Figure 11. This is a stainless steel chamber with a metal isolation valve of the type described by Ullman in Reference 11. With the exception of the rubber seal on the tubulated ionization gage, all gaskets are copper or gold. The liquid nitrogen cooled elbow prevented any apparent migration of the diffusion pump oil into the chamber even when operated at 250°K, so this temperature was maintained to avoid cryopumping water vapor on the elbow.

The mass spectrometer was used to measure the rate of change of pressure after the isolation valve was closed. It was found that the pressure rise was very non-linear, indicating significant adsorption was occurring. Figure 12 shows some typical pressure rise curves for H₂, N₂ and H₂O. Again the pressure is the equivalent nitrogen pressure. Included in the plots are the theoretical pressure rise rates based on a theoretical system pumping speed of 200 L/sec for nitrogen. The values for the other gases have been calculated from

$$S_{\text{gas}} = 200 \sqrt{\frac{28}{M_{\text{gas}}}} \quad (35)$$

Since the measured pressure rise rate is small compared to theoretical one, it is clear that either the pumping speed is greatly in error or the adsorption rate is of the same order as the pumping speed. Since the pumping speed is believed to be accurate to 20%, it is concluded that the adsorption rate is high.

While this data is difficult to analyze quantitatively, some qualitative comments can be made.

If the adsorption rate was constant, the pressure change would be an exponential function of time.

$$\frac{P - P_o}{P_f - P_o} = \left[1 - \exp \left(- \frac{S_A}{V} t \right) \right] \quad (36)$$

Since no value of final pressure (P_f) was found that would yield a constant value of adsorbent pumping speed for these time intervals, it was concluded that the adsorption rate decreased with an increase in the quantity adsorbed. This decrease in pumping speed probably results from the decreasing number of sites available for pumping as the gases are adsorbed. As discussed earlier, if this decrease is linear with the quantity pumped, the pressure should also be linear with the quantity pumped. If the outgassing rate is constant during this process, the quantity pumped is nearly linear with time, so the pressure rise should also be linear with time. It is seen that while this is approximately the case for N_2 , the other gases show a non-linear behavior.

If instead of adsorption the process depends upon the gases diffusing into the walls, then as shown in Reference 5, page 75, the surface concentration and therefore the chamber pressure will vary with the square root of the pumping time. Thus a plot of log pressure versus log time should have a slope of $1/2$. It is found that the slope varies both above and below $1/2$ so the diffusion process is not the only process involved. This is the same problem that exists in outgassing where it is often found that the data does not fit either a simple desorption process or a simple diffusion process.

Another complication in analyzing this data is the lack of knowledge of the effect of the adsorption history on the rate of adsorption since it is found that the adsorption process depends upon the quantity previously adsorbed, the rate of adsorption

and the time interval since the prior adsorption. In the present case it is possible that reliable results would require extremely long time intervals between opening the valve after obtaining one pressure rise curve and closing the valve to obtain another pressure rise curve. As noted before, this time interval will also be crucial in determining the usefulness of the dynamic continuously pumped system of obtaining outgassing data, since if the time required to establish equilibrium with the adsorption process is long compared to the time required for a significant change in outgassing rate, the results for this type of measurement will always be influenced by the adsorption. It seems possible that an analysis of the type presented in this report for determining the effect of the exposure history on the diffusion process could also be applied to the adsorption process once the dynamics of the adsorption are understood. Experiments that are designed to study the adsorption process would be required in order to guide the theoretical development. Since the present tests were made to determine the suitability of the constant volume process for determining outgassing rates, these tests results are not sophisticated enough to be useful in an adsorption analysis.

Since the high adsorption rate made the pressure rise curves unsuitable for determining the outgassing rate the present results have been used to determine the chamber outgassing rate using the equilibrium pressure (P_0 , nitrogen equivalent) and the assumed pumping speed. The results are presented in Figure 15. While the chamber contains about 2.0 cm^2 of mild steel surface and 100 cm^2 of copper, the outgassing rate has been computed on the basis of the stainless steel shell which has an area of 8900 cm^2 . Since this data was taken while the constant volume tests were being made, the results may be influenced by adsorption, but the level of the results for H_2 are comparable to those obtained in Reference 6 and the outgassing rates based on the total pressure are in the range found in the literature. The outgassing rates are considerably higher than values obtained in two other stainless

steel systems which gave outgassing rates in the 10^{-10} torr Liter/sec cm^2 range. Since both of these other systems had been pumped down many times, it is assumed that the differing of chamber histories was a significant factor in the lowered outgassing rate.

SUMMARY

A theoretical study was made of the factors involved in varying the outgassing rate of specimens exposed to vacuum conditions. Since part of the outgassing process appeared to be a diffusion process, the analogy was made between a vacuum system with diffusion controlled outgassing, and the problems of diffusion in heat transfer. It was shown that many existing heat transfer solutions are applicable to the analysis of outgassing processes.

It was found that the conventional baking technique is the most practical means of reducing the outgassing rate. The baking serves to temporarily increase the outgassing rate, and thus reduce the quantity of gas near the surface of the specimen. When the specimen is cooled, the outgassing rate is reduced due to this reduced concentration of gas.

An analysis was made of the increase in diffusion controlled outgassing rate that could be obtained by delivering the baking heat to the specimen in a series of high heat flux short duration pulses. As was anticipated, if the pulses were short enough, the surface temperature could be temporarily maintained well above the average specimen temperature, but in order for the outgassing rate to be significantly affected, the required pulse time had to be on the order of 10^{-7} sec. Since this short pulse time required a heat flux that was extremely high, it was concluded that the process was not a practical means of increasing the efficiency of the baking process.

Since it is not practical to bake a chamber before each test, it was necessary to determine the effect of using the chamber to store, bake or fix varying periods of time. An analysis was made of the effect of exposing a specimen alternately to a contaminating

atmosphere and a vacuum. It was found that the theoretical variation of the slope of the log outgassing rate versus log pumping time could have values between 0 and $3/2$, depending upon the exposure history. This is in contrast to the value of $1/2$ that is calculated for the slope of a system with uniform initial conditions.

Two experimental programs were conducted to measure the rates and the species of the outgassing from metal surfaces. One program using a cryopump surrounding the specimen was only partially successful due to some experimental difficulties that could not be corrected in the time available for testing. A second program made a comparison between the outgassing rate determined from the pressure rise rate in a closed system, and the outgassing rate determined from the equilibrium pressure attainable with a constant pumping speed. It was found that such large quantities of gas were re-adsorbed during the closed system measurements that the resulting outgassing rates were not valid. The results from the constant pumping speed measurements were in agreement with other values reported in the literature. It was found that the bulk of the outgassing was composed of H_2O , H_2 and N_2 .

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NOMENCLATURE

A	Surface area (length^2)
C	Molecular concentration (molecules/ length^3)
c	Specific Heat (cal/gr - $^{\circ}\text{K}$)
D	Diffusion coefficient ($\text{length}^2/\text{time}$)
E	Activation energy (cal/mole)
H	Surface heat transfer coefficient (cal/ length^2 - $^{\circ}\text{K}$)
K	Thermal conductivity (cal/ length - $^{\circ}\text{K}$)
L	Plate thickness in the x direction
M	Molecular mass
N	Outgassing rate (molecules/ length^2 - time)
N _A	Avagadro: No. (6.02×10^{23} molecules/mole)
P	Pressure (torr)
q	Heat flux (cal/ length^2 - time)
R	Gas constant (1.986 cal/mole)
S	Pumping speed ($\text{length}^3/\text{time}$)
S _A	Adsorption pumping speed
T	Temperature ($^{\circ}\text{K}$)
t	Time
v	Temperature increase
V	Volume (length^3)
x	Coordinate normal to the wall
ρ	Density (gr/ length^3)
k	Thermal diffusivity ($\text{length}^2/\text{time}$)

τ Period of heating cycle
 $\phi \quad \frac{1}{C_y} = 0 \quad \frac{S}{A} \text{ (length/time)}$
 C_{gas}

$\eta \quad \int_0^t D \, dt$

ω Fraction of surface covered by adsorbed molecules.

Subscript

o Initial conditions
 s Surface conditions

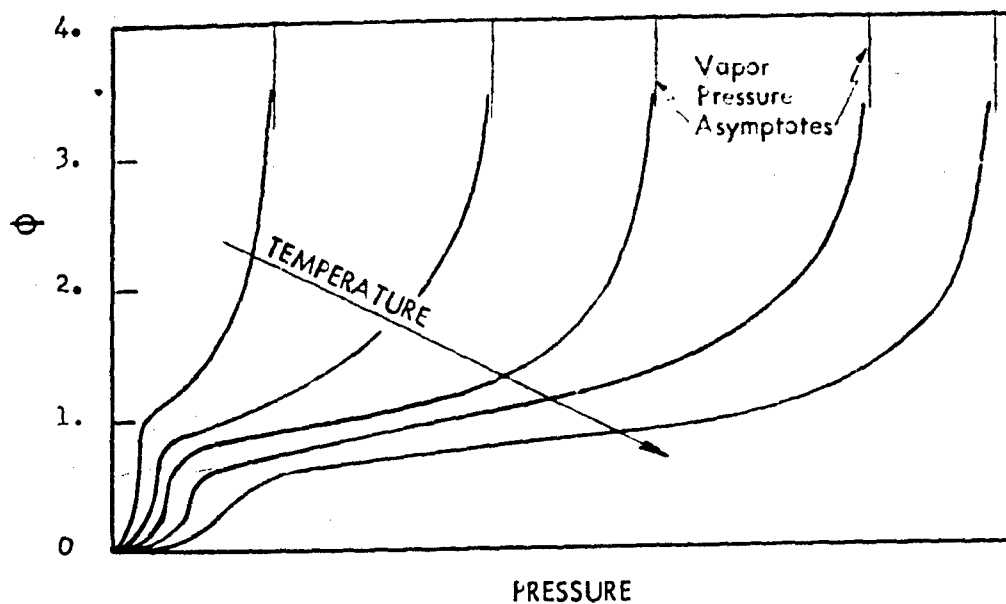


FIGURE 1, ONE TYPE OF VARIATION OF SURFACE COVERAGE WITH GAS TEMPERATURE AND PRESSURE ($\Theta = 1$ Corresponds to one monolayer)

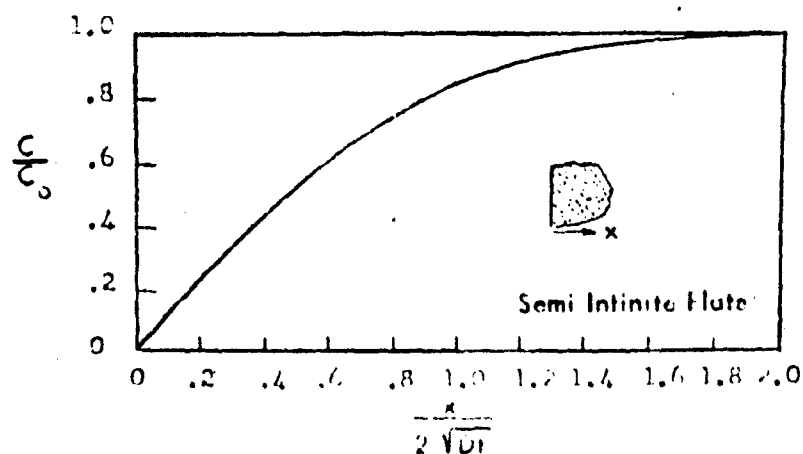


FIGURE 2, VARIATION IN CONCENTRATION WITH DEPTH INTO PLATE AND PUMPING TIME

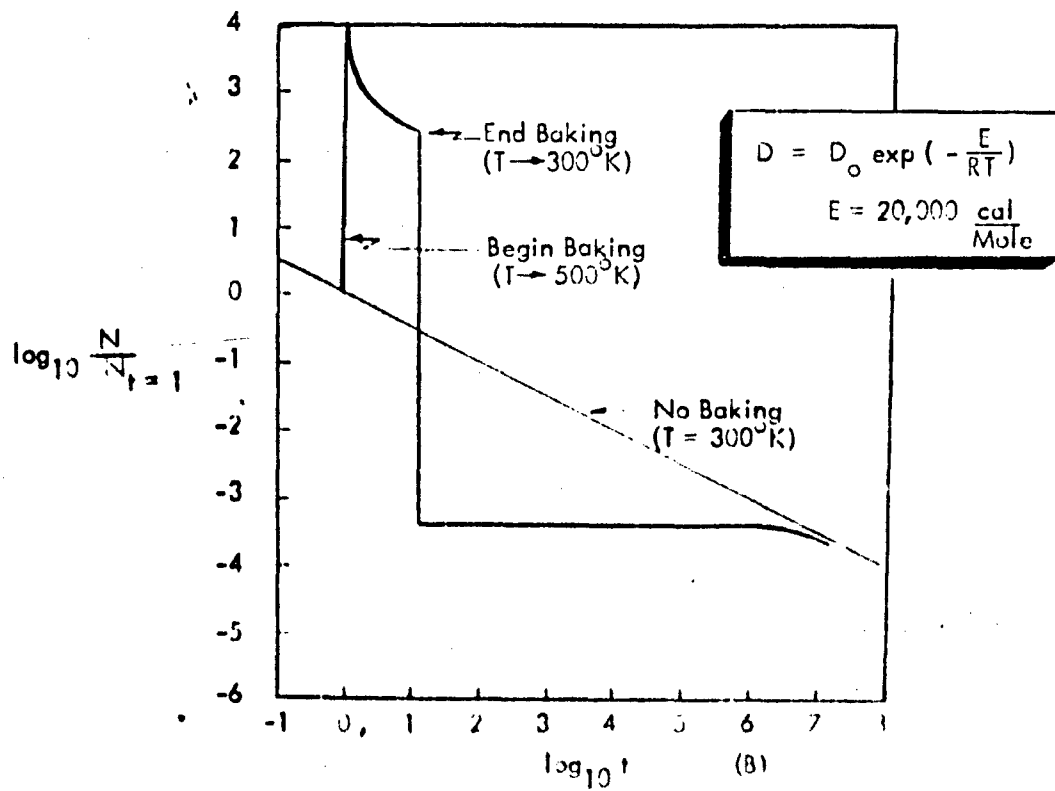
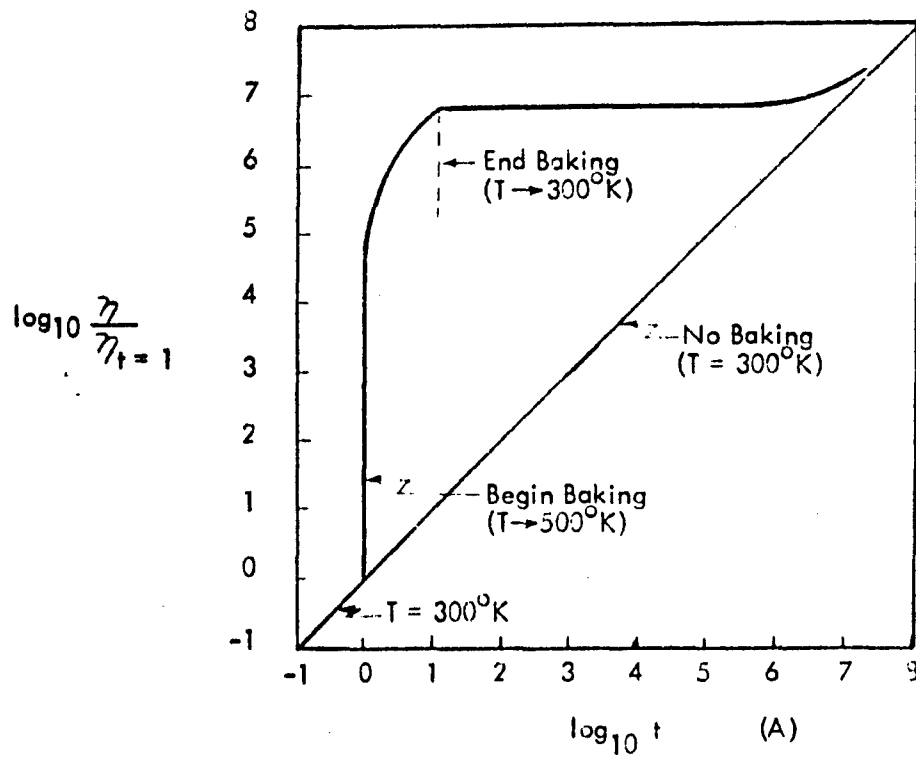


FIGURE 3, EFFECT OF BAKING ON η AND OUTGASSING RATE

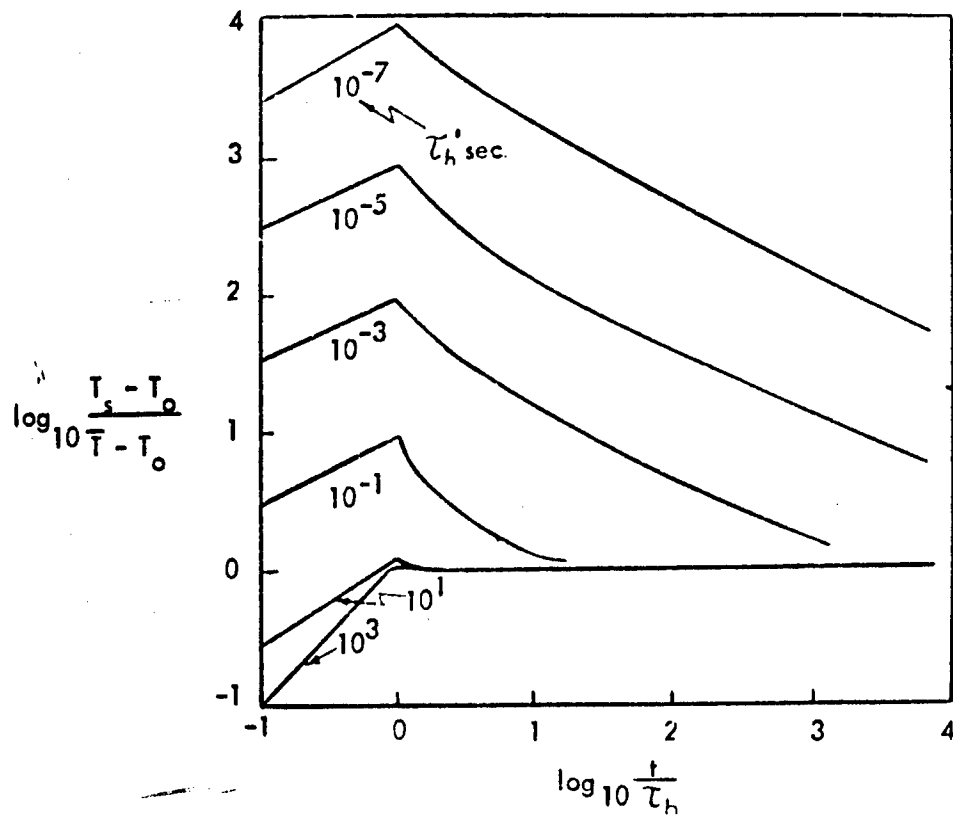


FIGURE 4, VARIATION OF SURFACE TEMPERATURE RISE WITH LENGTH OF HEATING PULSE. (1/4" Stainless Steel Plate)

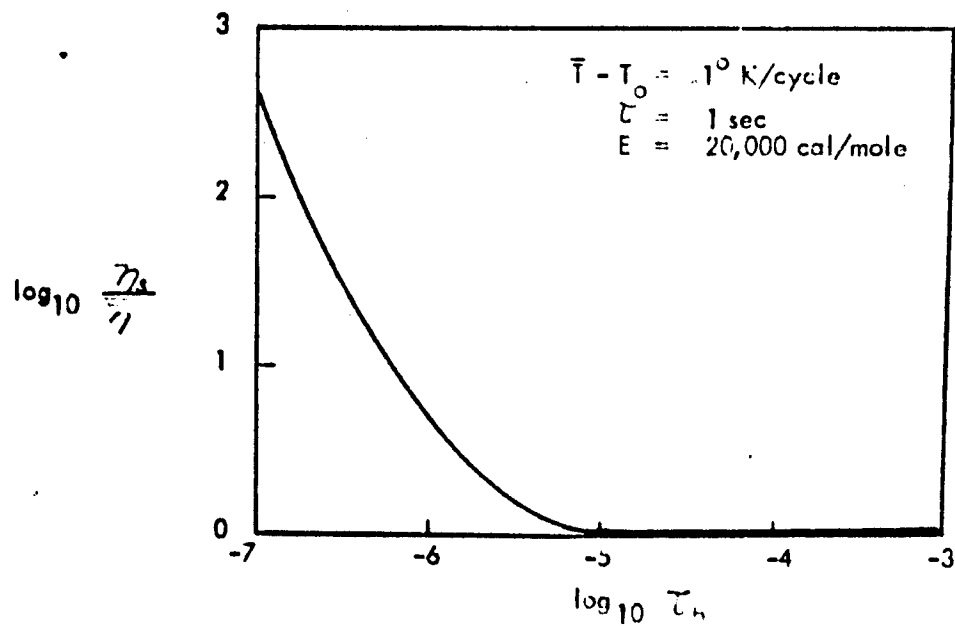


FIGURE 5, VARIATIONS OF $\frac{\eta_s}{\eta}$ WITH LENGTH OF HEATING PULSE

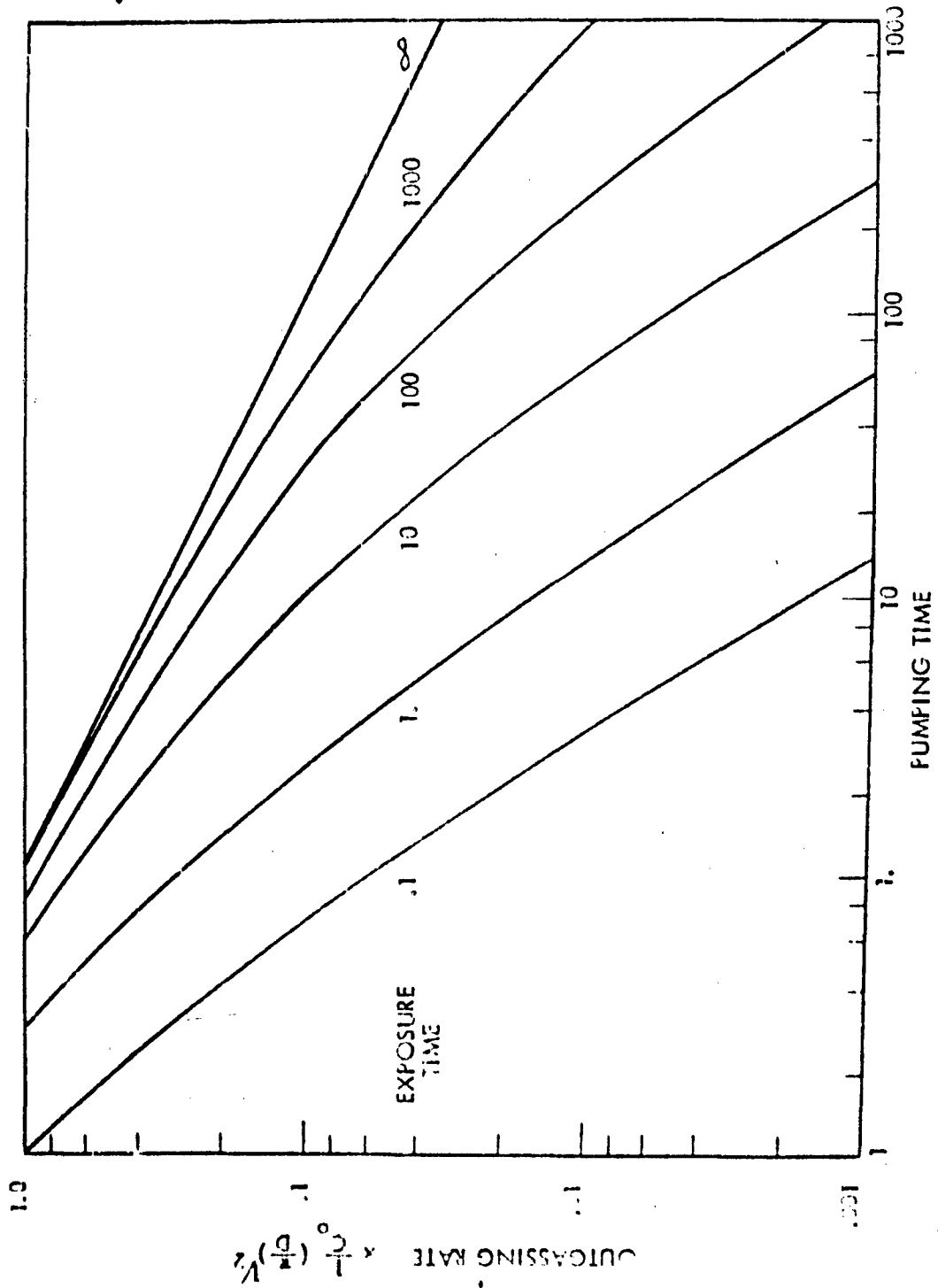


FIGURE 6, VARIATION IN OUTGASSING RATE WITH EXPOSURE TIME FOR AN INITIALLY OUTGASSED SYSTEM
(time any consistent units)

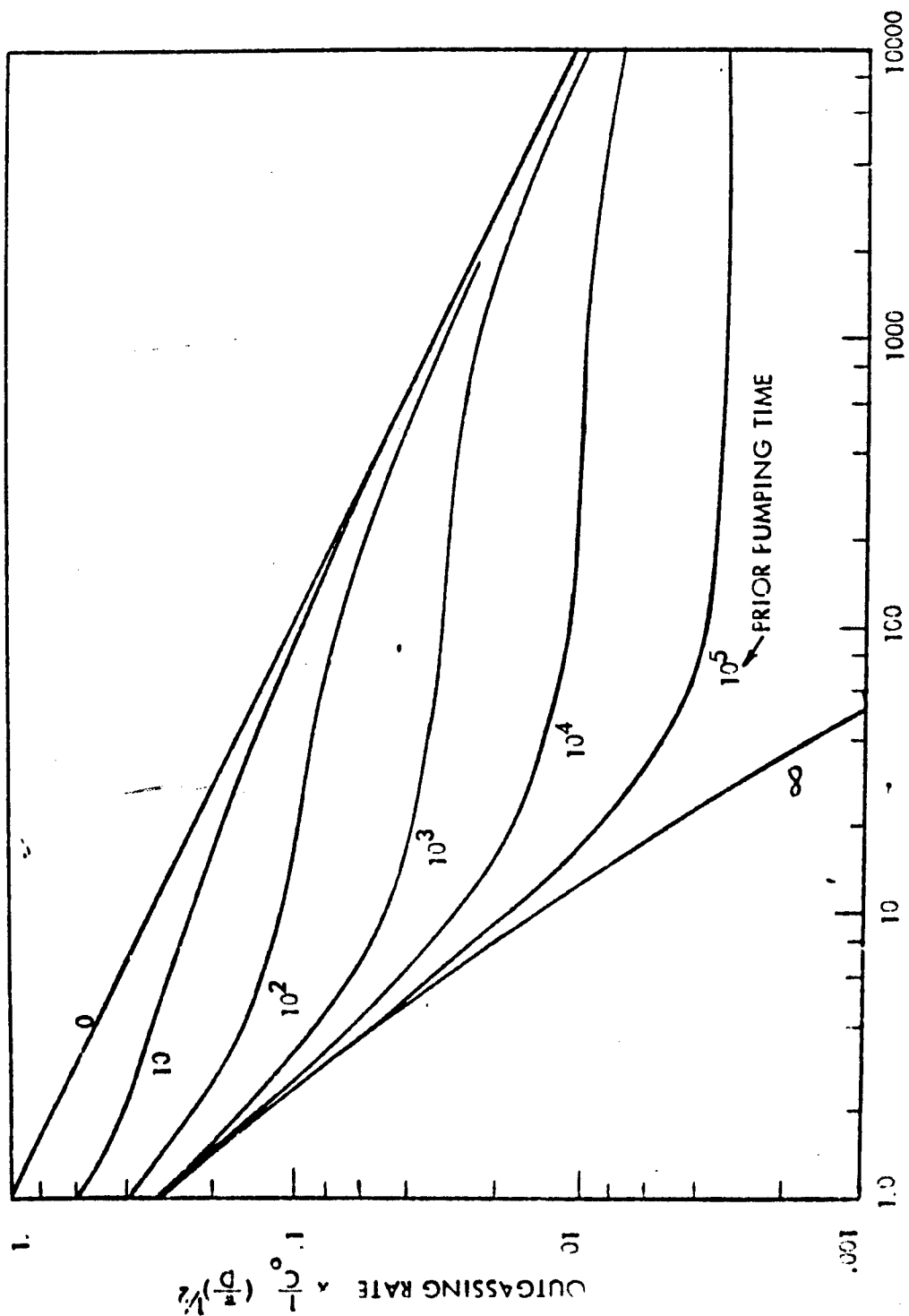


FIGURE 7, VARIATION IN OUTGASSING RATE WITH PRIOR PUMPING TIME FOR A SYSTEM
WITH A UNIFORM INITIAL CONCENTRATION
(time any consistent units)

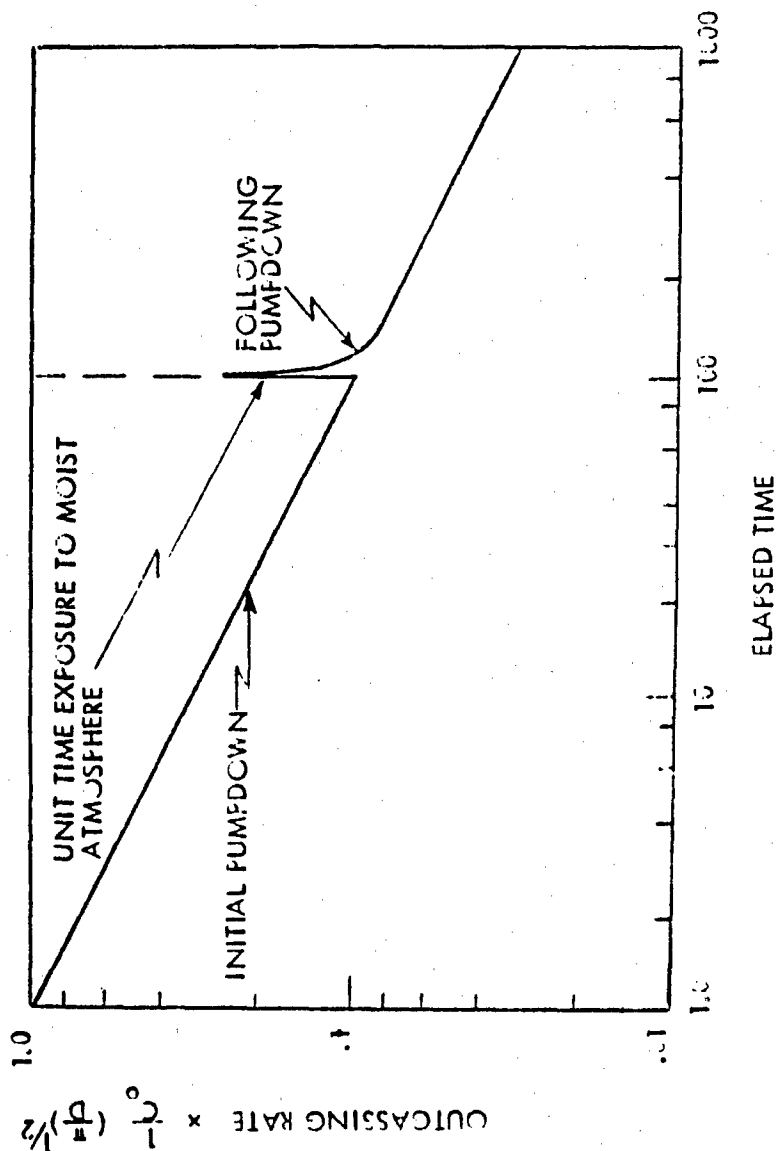


FIGURE 3, VARIATION IN OUTGASSING RATE WITH TOTAL ELAPSED TIME
(time any consistent units)

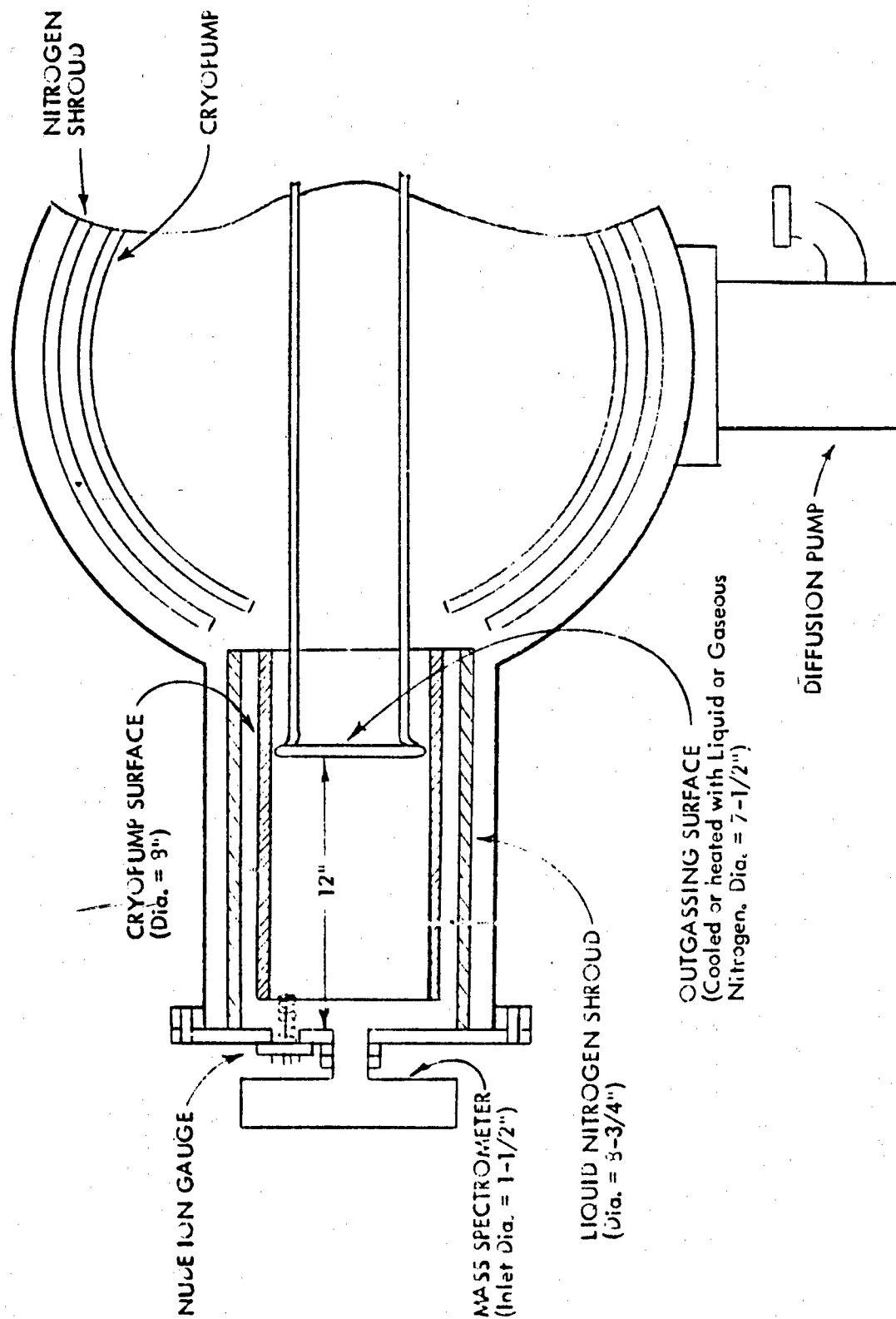


FIGURE 2, EXPERIMENTAL ARRANGEMENT USING A CRYOPUMPING SURFACE

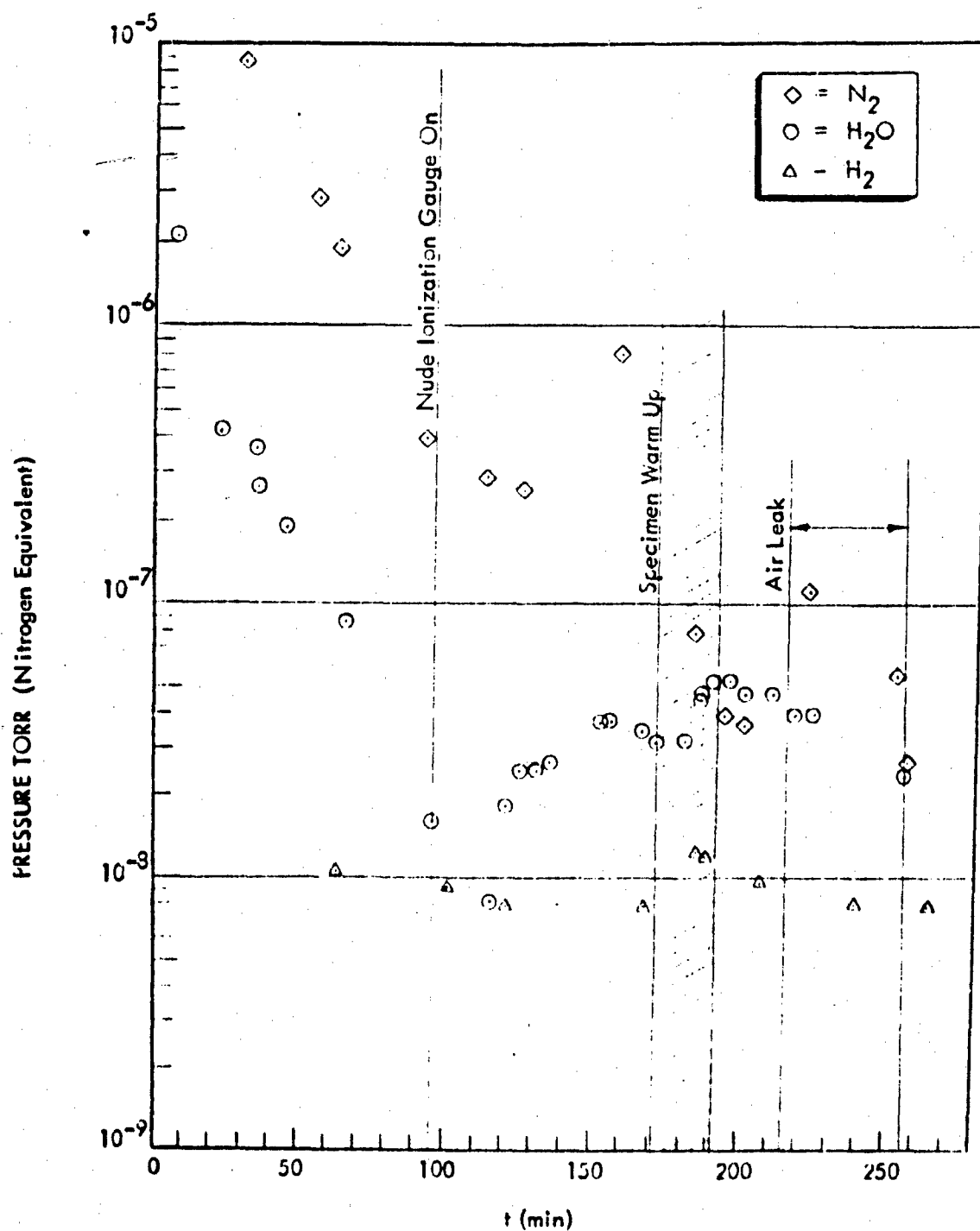


FIGURE 10, VARIATIONS OF MASS SPECTROMETER PRESSURE DUE TO OPERATING NUDE IONIZATION GAUGE AND WARMING UP SPECIMEN (zero time arbitrary)

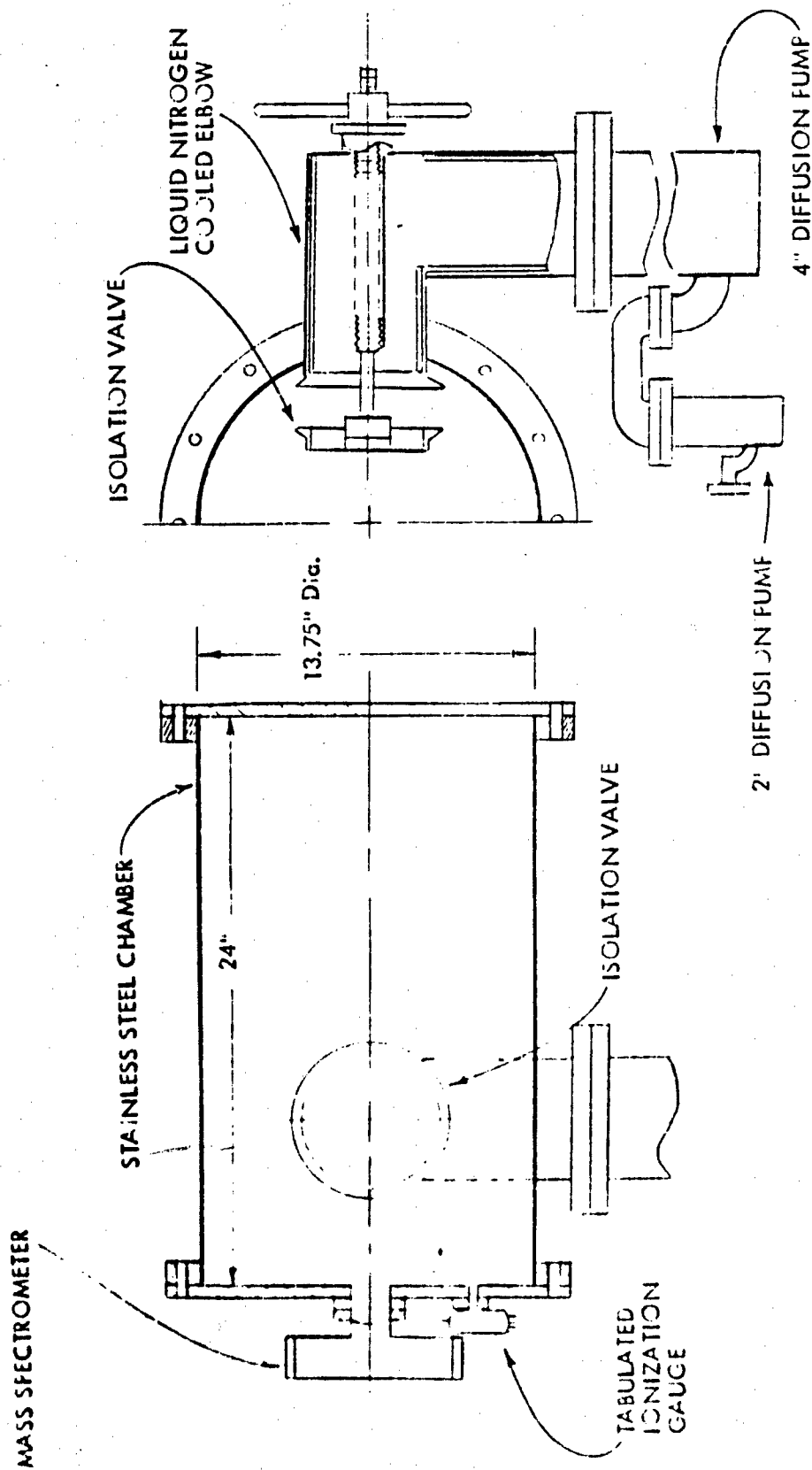


FIGURE 11, EXPERIMENTAL ARRANGEMENT OF STAINLESS STEEL CHAMBER WITH ISOLATION VALVE

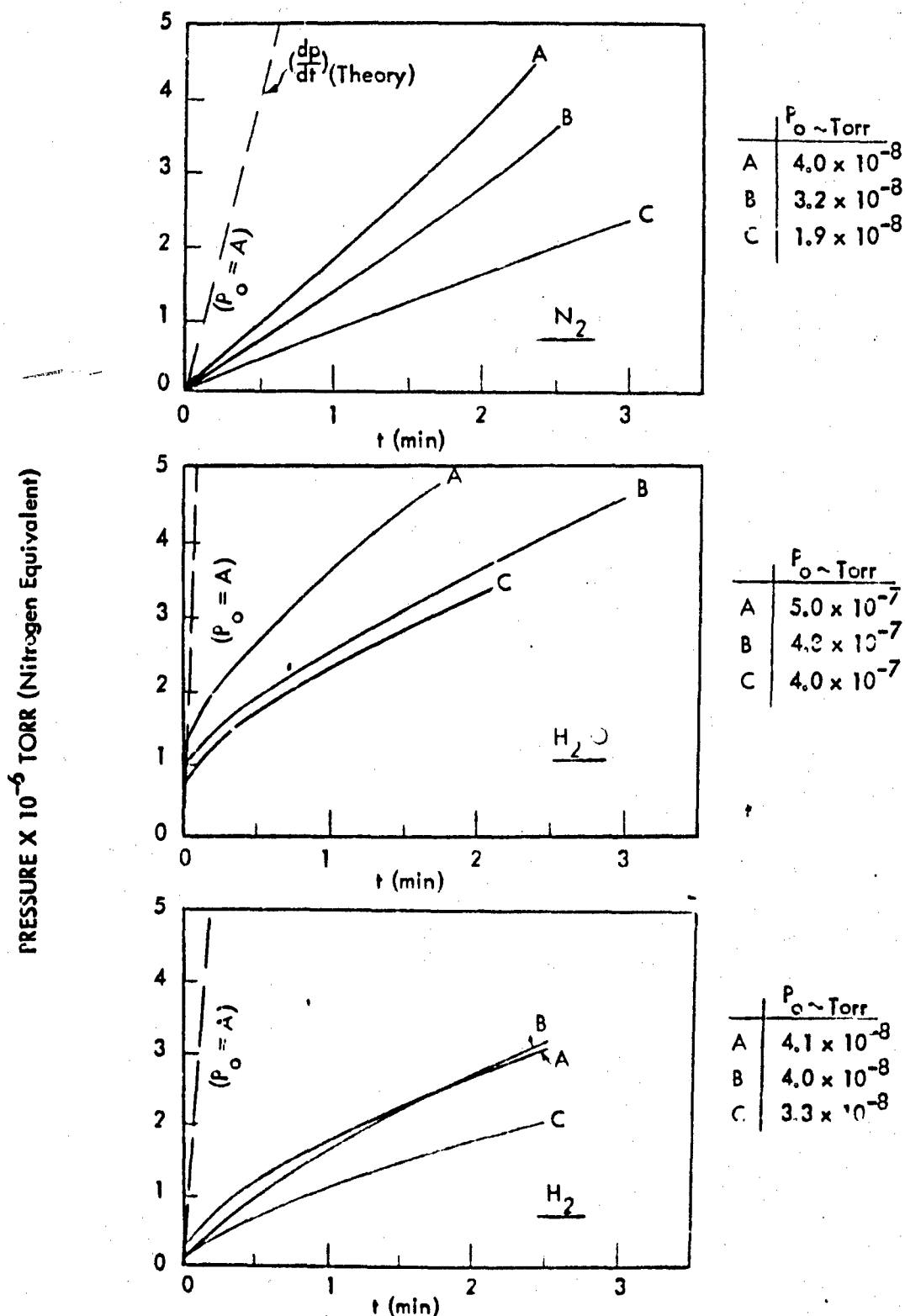


FIGURE 12. TYPICAL PARTIAL PRESSURE RISE FOR N_2 , H_2O AND H_2 WHEN THE SYSTEM IS ISOLATED FROM THE PUMPING SOURCE. (A, B, and C are the partial pressures in the system at the time of isolation).

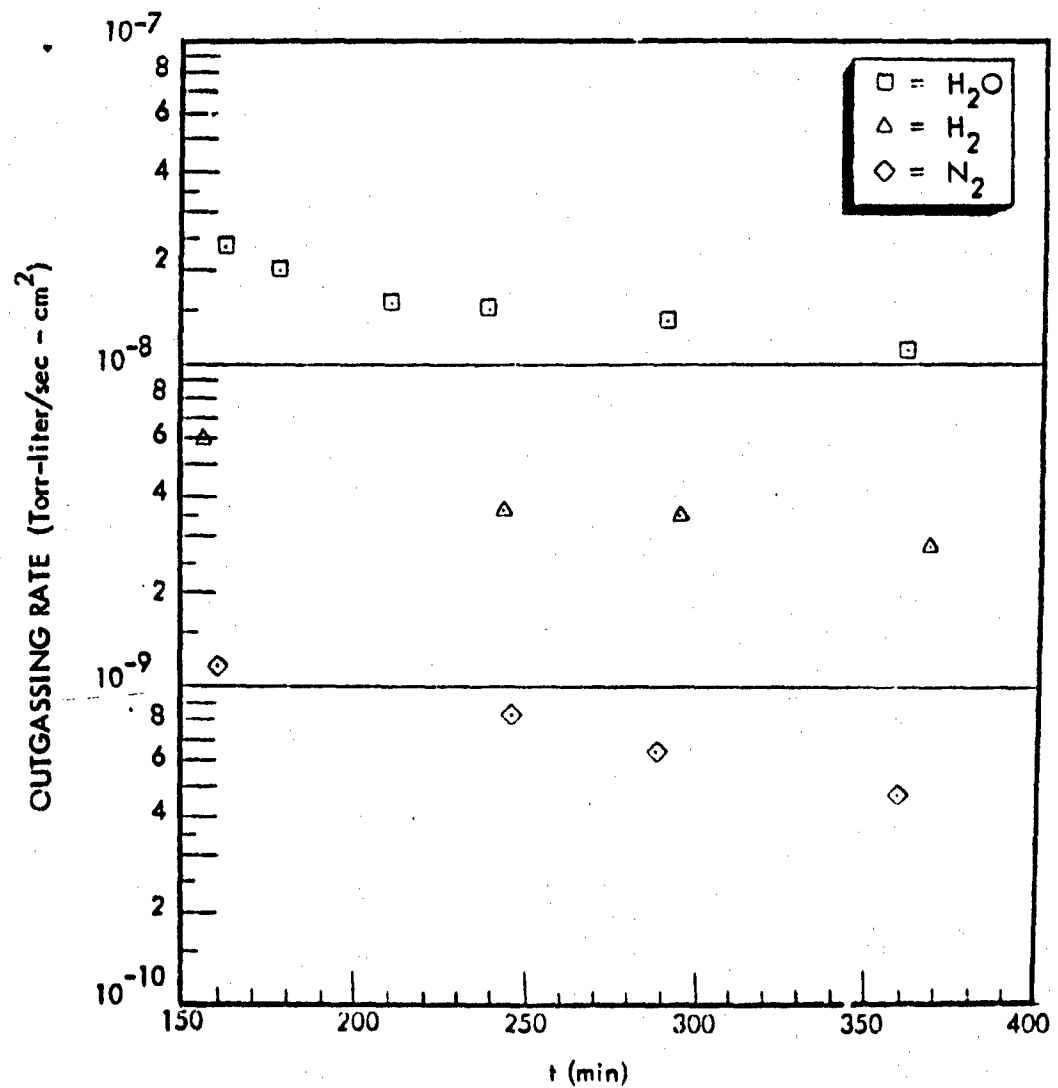


FIGURE 13, VARIATION OF OUTGASSING RATE WITH PUMPING TIME.
(Rate computed from theoretical system pumping speed for each specimen)